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STABILITY OF LYOPHOBIC COLLOIDS, XI

Investigations on the Stability of the Hydrous Ferric Oxide Sols
as related to the Coagulating Powers of
the Poly-valent Precipitating Ions.

By KRISHNA CHANDRA NAND AND SATYESHWAR GHOSH

It has been shown that simple Whetham's rule is only a first approximation for the ratios of the precipitating values of ions of varying valencies. Modifications of Whetham's rule have been deduced by S. Ghosh and also by Verwey and Overbeek on the electrostatic properties and also on the effect of electrolyte on the surface potential or the electric charge on the colloidal particles. These modifications have been critically examined here for the sols of hydrous ferric oxide at the varying dielectric constants of the dispersing medium at the different lengths of the time allowed for the contact of sol with the electrolyte. Our results show that in actual practice the relation of S. Ghosh or Verwey and Overbeek cannot be realised in a true sense because the sol is likely to coagulate, when the charge and hence, the surface potential becomes zero. But we have observed that the ratio of the precipitating ions of different valencies should decrease, as the charge on the colloidal particles decreases and it is well known that the stability of a sol decreases with increasing purity.

Introduction

The precipitation values of an electrolyte are related to the valencies of the coagulating ions and the precipitation values or the inverse of the coagulating powers of an electrolyte is determined for the purpose of judging the stability of a sol. The precipitation values of an electrolyte has long been investigated and Schulze and Hardy¹⁾ and others²⁾ pointed out the importance of valency of the oppositely charged ion. Whetham³⁾ obtained a simple relation, that the precipitating concentrations of a series of coagulating ions are proportional to a constant raised to the power representing the valency of each ion. If the precipitation concentrations of mono-, bi-, tri- and polyvalent coagulating ions are $P_1, P_2, P_3, \dots, P_n$ then,

$$P_1 : P_2 : P_3 : \dots : P_n = 1 : X : X^2 : \dots : X^{n-1}$$

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- 1) H. Schulze, *J. Prakt. Chem.*, 25, 431 (1882); 27, 320 (1883); 32, 390 (1884)
W. Hardy, *Proc. Roy. Soc.*, 66, 110 (1899); *J. Phys. Chem.*, 4, 235 (1900)
- 2) W. Ostwald, *Kolloid Z.*, 26, 28, 59 (1920)
- 3) W. C. D. Whetham, *Phil. Mag.*, 5, 48, 474 (1899)

where 'X' is less than unity. This relation is rarely found to tally with the experimental data. Modifications of this relation has been suggested by S. Ghosh⁵⁾ and also by Verwey and Overbeek¹⁰⁾¹¹⁾.

De Boer⁶⁾, Hamaker⁸⁾ and others⁴⁾⁷⁾⁹⁾ and later Verwey and Overbeek (*loc cit.*) considered the interaction of two electrically charged colloidal particles, having a double layer. They have computed the potential curves as two electrically charged particles approach each other. The nature of such potential curves depends on the values of attractive and repulsive potential energy. The attractive potential energy (V_A) between two parallel plates having the thickness much greater than their distance of separation is given by

$$V_A = \frac{-A}{48\pi d^2} \dots\dots\dots (1)$$

A is a constant characteristic of the dispersed particles and d is half the distance of separation of plates.

Further, the repulsive potential energy, when the double layer interaction is not very extensive, of two parallel plates, each one square centimeter in area, is

$$V_R = \frac{32nkT\gamma^2}{X}(1 - \tanh Xd) \dots\dots\dots (2)$$

where, n is the number of ions of opposite charge to the particle contained in one centimeter of intermicellar solution, X is a parameter related to the reciprocal of the effective thickness of the electrical double layer, k is the Boltzmann constant, T being the absolute temperature and

$$\gamma = \frac{\exp(Ze\psi_0/2kT) - 1}{\exp(Ze\psi_0/2kT) + 1} \dots\dots\dots (3)$$

in which Z is the valency of the counter ions, e the charge on the electron, ψ_0 is the potential existing between the surface of the particle and the intermicellar solution. The parameter X in the above equation is more precisely defined as $\left(\sqrt{\frac{8\pi ne^2 Z^2}{\epsilon kT}}\right)$, where ϵ stands for the dielectric constant of the intermicellar solution. Thus, the resultant potential energy (V) arising out of the attractive and the repulsive potentials is given by

$$V = \frac{32nkT\gamma^2}{X}(1 - \tanh Xd) - \frac{A}{48\pi d^2} \dots\dots\dots (4)$$

4) H. B. G. Casimir and D. Polder, *Phys. Rev.*, **73**, 360 (1948)

5) cf. M. M. Chakravarty, S. Ghosh and N. R. Dhar, *J. Phys. Chem.* **34**, 326 (1930)

6) J. B. De Boer, *Trans. Faraday Soc.*, **32**, 21 (1936)

7) B. Dejaguin, *Trans. Faraday Soc.*, **36**, 20, (1940)

8) H. C. Hamaker, *Rec. Trav. Chim.*, **55**, 1015 (1936); **56**, 3, 727 (1937)

9) I. I. Langmuir, *J. Chem. Phys.*, **6**, 893 (1938)

10) E. J. Verwey and J. Th. Overbeek, "Theory of the Stability of Lyophobic Colloids.", Amsterdam (1948)

11) E. J. Verwey and J. Th. Overbeek, *Trans. Faraday Soc.*, **42B**, 117 (1946); *Philips Research Repts.* **1**, 33 (1945)

It is clear that the necessary condition for a sol to be stable is $V_R > V_A$ and that V should have a positive value. Further, for commencement of the flocculation, the necessary condition is that $V=0$ and $\frac{dV}{dd}=0$ and thus they obtained

$$n = \frac{107\epsilon^3 k^6 \gamma^4}{A^2 (Ze)^6} \dots\dots\dots (5)$$

at 25°C, when the dispersed particles are in water, dielectric constant is 78.44, hence, for a Z - Z valent electrolyte equation leads to the precipitation value C in millimoles per litre,

$$C = 8.10^{-22} \frac{\gamma^4}{A^2 Z^6} \dots\dots\dots (6)$$

When the surface potential is high and approaches to unity being independent of valency, the precipitation values of the mono-, di-, and trivalent ions appear as

$$1 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6 \text{ or } 100 : 1.6 : 0.13, \dots\dots\dots (7)$$

When the surface potential is very low, the value of γ^4 reduces to $\frac{Ze\phi_0/2kT\gamma^4}{2}$ so that

$$C = 8.10^{-30} \frac{\phi_0^4}{A^2 Z^2} \dots\dots\dots (8)$$

Thus, for such a case the ratio of the precipitation values reduces to:—

$$1 : \left(\frac{1}{2}\right)^2 : \left(\frac{1}{3}\right)^2 \text{ or } 100 : 25 : 11.11, \dots\dots\dots (9)$$

In other words, therefore, the ratio of the precipitation values varies within these limits (7) and (9).

S. Ghosh (*loc. cit.*) considered the interaction on the oppositely charged ion and a colloidal particle shielded by a double layer of the oppositely charged ions. According to him, the oppositely charged ions have a barrier to cross arising out of the double layer before it can become operative in the charge neutralisation on the colloidal surface. Thus, he pointed out that if other factors, such as specific adsorption of the coagulating ions or that of similarly charged ions available from the electrolyte do not complicate the process, the precipitation values should be in the ratio of

$$1 : \frac{1}{2}\alpha : \frac{1}{3}\alpha^2 \dots\dots\dots (10)$$

The value of α is given by the factor

$$e^{-Qe/\epsilon r k T} \dots\dots\dots (11)$$

Q being the electrical charge on the colloidal particles and r the thickness of the double layer. Hence, if Q decreases the value of α tends to be unity, the ratio approaches the value of

$$1 : \frac{1}{2} : \frac{1}{3} \text{ or } 100 : 50 : 33.3 \dots\dots\dots (12)$$

We have critically examined the applicability of both these modifications of Wetham's rule in the light of the variation of the dielectric constant of the dispersing medium.

Experimental

For the proposed study, the three samples A, B and C of the hydrous ferric oxide sols containing 3.6296 gm. of Fe^{+++} /litre, their pH. and purities being 2.2, 3.6, 4.5 and 3.7642, 11.6348, 19.6897 respectively, were prepared by the Graham method and the coagulation at different values of the dielectric constant of the dispersing medium was determined as already described¹²⁾. In the following tables the precipitating values for mono-, bi-, and trivalent coagulating ions have been reproduced. For convenience the precipitation value of monovalent ion is taken as 100 and the values of α of the relation suggested by S. Ghosh has been calculated (α_1 refers to the values for di/mono and α_2 to that of tri/di valent coagulating ions). These values have been calculated for different lengths of the time of coagulation viz., one hour and two hours and also for infinite time of observation in order to show how these values of α_1 and α_2 and the ratio of the precipitation values vary with the time of observation.

Results and Discussion

A perusal of the data recorded leads to the following conclusions:

1. For the sols containing greater amounts of free peptising agents, the ratio of the coagulating ion is found to be smaller and the ratio tends to increase with decreasing amount of the stabilising ions. In other words, in the sols which were subjected to dialysis, the free electrolyte present in the system dialyses out and thus, the sol acquires greater purity. In such cases, the ratio of mono-, bi- and trivalent coagulating ions is found to increase with the increasing purity of the sol.
2. The ratio of the precipitating values of mono-, bi- and trivalent coagulating is also found to vary with the dielectric constant of the dispersing medium, so that ratio increases with a decrease in the dielectric constant and vice versa.
3. The ratio is also dependent on the time allowed for coagulation, that is, when the time of coagulation is small as brought about by larger amounts of the coagulating electrolyte, the ratio is found to be greater, when compared with one, for infinite time of coagulation, where the process of coagulation is at its slowest.
4. The values of α_1 or the ratio of divalent to monovalent coagulating ions, tend to increase with a decrease in the dielectric constant of the dispersing medium and the reverse is the case for an increase in the values of dielectric constant, showing thereby that the values of α_1 decrease with the increasing stability of a sol.
5. It is interesting to note here that the value of α_1 is smaller for the sol sample, which is

12) K. C. Nand and S. Ghosh, *Proc. Natl. Acad. Sci. India* (Communicated)

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Ratios of precipitating concentrations of mono-, bi-, and trivalent coagulating ions and corresponding values of α_1 and α_2 as obtained from their precipitation values for one hour time of coagulation

Table 1 Sol sample (A)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	6.7	0.250	0.134	0.0560
50.52	100	6.3	0.222	0.126	0.0530
59.24	100	5.8	0.200	0.116	0.0517
67.98	100	5.5	0.174	0.110	0.0475
71.19	100	5.2	0.150	0.104	0.0432
76.76	100	4.8	0.122	0.096	0.0381
77.32	100	4.4	0.100	0.088	0.0341
77.92	100	4.0	0.080	0.080	0.0300
79.29	100	3.7	0.060	0.074	0.0248
80.88	100	3.4	0.040	0.068	0.0177
82.54	100	3.0	0.020	0.060	0.0100

Table 2 Sol sample (B)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	7.8	0.255	0.156	0.0983
50.52	100	7.3	0.240	0.146	0.0835
59.24	100	7.0	0.224	0.140	0.0715
67.98	100	6.6	0.210	0.132	0.0630
71.19	100	6.2	0.194	0.122	0.0550
76.76	100	5.8	0.180	0.116	0.0465
77.32	100	5.5	0.164	0.110	0.0443
77.92	100	5.1	0.148	0.102	0.0435
79.29	100	4.7	0.125	0.094	0.0400
80.88	100	4.3	0.106	0.066	0.0370
82.54	100	4.0	0.080	0.080	0.0300

Table 3 Sol sample (C)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	9.0	0.340	0.180	0.0567
50.52	100	8.5	0.310	0.170	0.0547
59.24	100	8.0	0.288	0.160	0.0525
67.98	100	7.6	0.250	0.152	0.0500
71.19	100	7.2	0.235	0.144	0.0498
76.76	100	6.8	0.220	0.136	0.0485
77.32	100	6.5	0.204	0.130	0.0471
77.92	100	6.0	0.187	0.120	0.0468
79.29	100	5.6	0.172	0.112	0.0460
80.88	100	5.2	0.155	0.104	0.0447
82.54	100	4.8	0.138	0.094	0.0431

Ratios of the precipitating concentrations of mono-, bi-, and trivalent coagulating ions and corresponding values of α_1 and α_2 as obtained from their precipitation values for two hour time of coagulation

Table 4 Sol sample (A)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	5.2	0.135	0.104	0.0390
50.52	100	4.8	0.120	0.096	0.0375
59.24	100	4.5	0.108	0.090	0.0360
67.98	100	4.2	0.098	0.084	0.0350
71.19	100	3.9	0.084	0.078	0.0335
76.76	100	3.6	0.070	0.072	0.0291
77.32	100	3.3	0.058	0.066	0.0264
77.92	100	3.0	0.042	0.060	0.0210
79.29	100	2.7	0.034	0.054	0.0190
80.88	100	2.4	0.026	0.048	0.0146
82.54	100	2.2	0.014	0.044	0.0095

Table 5 Sol sample (B)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	6.2	0.188	0.124	0.0455
50.52	100	5.8	0.170	0.116	0.0440
59.24	100	5.5	0.156	0.110	0.0426
67.98	100	5.2	0.140	0.104	0.0404
71.19	100	4.9	0.124	0.098	0.0383
76.76	100	4.6	0.110	0.092	0.0358
77.32	100	4.3	0.095	0.086	0.0332
77.92	100	4.0	0.080	0.080	0.0300
79.29	100	3.7	0.064	0.074	0.0262
80.88	100	3.4	0.058	0.068	0.0256
82.54	100	3.2	0.047	0.064	0.0220

Table 6 Sol sample (C)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	7.1	0.215	0.140	0.0458
50.52	100	6.8	0.200	0.134	0.0445
59.24	100	6.5	0.188	0.130	0.0434
67.98	100	6.2	0.176	0.124	0.0428
71.19	100	5.9	0.162	0.118	0.0412
76.76	100	5.6	0.150	0.112	0.0395
77.32	100	5.3	0.136	0.106	0.0374
77.92	100	5.0	0.122	0.100	0.0366
79.29	100	4.7	0.112	0.094	0.0357
80.88	100	4.4	0.100	0.088	0.0340
82.54	100	4.2	0.098	0.084	0.0300

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Ratios of the precipitating concentrations of mono-, bi-, and trivalent coagulating ions and corresponding values of α_1 and α_2 as obtained from their precipitation values for infinite time of coagulation

Table 7 Sol sample (A)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	1.47	0.0200	0.0294	0.0200
50.52	100	1.35	0.0188	0.0270	0.0209
59.24	100	1.29	0.0182	0.0258	0.0211
67.98	100	1.24	0.0178	0.0248	0.0214
71.19	100	1.17	0.0172	0.0235	0.0219
76.76	100	1.10	0.0162	0.0220	0.0220
77.32	100	1.05	0.0156	0.0210	0.0223
77.92	100	1.00	0.0140	0.0200	0.0225
79.29	100	0.90	0.0136	0.0180	0.0227
80.88	100	0.85	0.0130	0.0170	0.0230
82.54	100	0.80	0.0125	0.0160	0.0234

Table 8 Sol sample (B)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	1.60	0.0245	0.0320	0.0230
50.52	100	1.53	0.0240	0.0306	0.0235
59.24	100	1.45	0.0235	0.0290	0.0240
67.98	100	1.41	0.0230	0.0282	0.0244
71.19	100	1.33	0.0220	0.0265	0.0243
76.76	100	1.25	0.0208	0.0250	0.0250
77.32	100	1.18	0.0200	0.0235	0.0255
77.92	100	1.10	0.0190	0.0220	0.0260
79.29	100	1.05	0.0185	0.0210	0.0264
80.88	100	1.00	0.0180	0.0200	0.0270
82.54	100	0.90	0.0174	0.0188	0.0290

Table 9 Sol sample (C)

Dielectric constant values	Precipitation values for			Values of	
	KCl	K ₂ SO ₄	K ₃ Fe(CN) ₆	α_1 (di/mono)	α_2 (tri/di)
41.71	100	1.89	0.0310	0.0358	0.0250
50.52	100	1.74	0.0297	0.0342	0.0255
59.24	100	1.65	0.0289	0.0330	0.0260
67.98	100	1.58	0.0280	0.0315	0.0266
71.19	100	1.50	0.0270	0.0300	0.0270
76.76	100	1.40	0.0261	0.0280	0.0280
77.32	100	1.31	0.0252	0.0261	0.0289
77.92	100	1.25	0.0242	0.0250	0.0295
79.29	100	1.18	0.0230	0.0235	0.0299
80.88	100	1.12	0.0224	0.0222	0.0304
82.54	100	1.05	0.0218	0.0210	0.0311

more stable and also for the sol containing greater amount of free peptising ions.

6. It is, however, seen that the values of α_2 or the ratio of the precipitation values of tri- to divalent coagulating ions also decrease with the increasing stability when the time of coagulation is one or two hour, but in the case of the infinite time of coagulation, the case is reversed.

7. It is also of interest to find that the values of the α_1 and α_2 are much the same in the absence of a non-electrolyte, when the time of coagulation is infinite but their values show some deviation in the presence of a non-electrolyte. Further, when the time of coagulation is less viz., one or two hours, the deviation in these values is still more marked, so much so that these values are different, even for pure water.

Thus it is obvious that from the considerations of both Verwey and Overbeek and of S. Ghosh on the process of coagulation by electrolytes, the ratio of mono-, bi-, and trivalent coagulating ions will approach nearer, with the decrease in the electric charge on the colloidal particles. It is, therefore, clear that the applicability of Whetham's rule or its modifications is dependent on several factors and the relation varies within wide limits. It has been pointed out by Verwey that although there exist numerous experimental data on the coagulation of hydrophobic sols, the rigorous test of the theoretical approach of this problem is not possible. The coagulation values have ordinarily been determined for a certain slow process, but as Verwey (*loc. cit.*) states that it is not known by what factor, slower than the ideal rapid one. In view of such facts we have examined the applicability of Whetham's rule under different conditions including the effect of time given to observe the complete coagulation. Undoubtedly the data for the infinite time allowed for coagulation are those, when the process is slowest, but is devoid of the effect of them. Further work will follow in subsequent publications.

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